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BUREAU OF STANDARDS

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RECOMMENDED SPECIFICATION FOR LIMESTONE,
QUICKLIME, AND HYDRATED LIME FOR USE IN
THE MANUFACTURE OF GLASS

This is the second of a series of specifications for the lime used in various chemical industries. To assist in the development of these specifications the Bureau has called together an Interdepartmental Conference on Chemical Lime, composed of representatives of the Geological Survey and Bureau of Mines of the Interior Department; the Bureau of Soils, Bureau of Chemistry, Forest Service, and Fixed Nitrogen Research Laboratory of the Department of Agriculture; and the Chemical Warfare Service of the War Department. The present specification, based on a draft originally prepared by A. E. Williams of the glass section, Bureau of Standards, has been unanimously approved by the above conference and has been adopted as tentative by a majority vote of the Standardization Committee of the Glass Division of the American Ceramic Society.

ABSTRACT

A general description of the use of lime in glass manufacture is followed by definitions of the terms "limestone," "quicklime," and "hydrated lime," and a statement as to the commercial packages in which these materials are marketed.

The quality of lime used in glass manufacture may vary. Any lime containing more than 83 per cent of the oxides of calcium and magnesium is suitable for glass manufacture, provided only that certain particularly deleterious substances are within reasonable limits. The composition should not vary from day to day more than 2 per cent. The material should all pass a No. 16 sieve.

Complete directions for sampling, testing, and retesting are included.

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1. GENERAL

(a) **USE OF LIME IN MAKING GLASS.**—Most common glasses are fused mixtures of alkali (usually soda), alkaline earth (usually lime), and silica. Freedom from color is important in determining the quality of glass, which, in turn, depends upon the absence of coloring oxides (usually iron) from the raw material.

Limestone, quicklime, or hydrated lime may be used for making glass. The decision as to which to use is generally based on availability, cost, and present practice.

(b) **DEFINITION OF LIMESTONE, QUICKLIME, AND HYDRATED LIME.**—Limestone consists essentially of calcium carbonate, or of calcium and magnesium carbonates where the amount of the latter does not exceed 45.5 per cent. Quicklime is the product resulting from the calcination of limestone and consists essentially of calcium oxide, or of calcium and magnesium oxides. It will slake when water is added to it, and this slaking is accompanied by an evolution of heat and an increase in volume. Hydrated lime is a dry powder which is made by treating quicklime with enough water to satisfy its chemical affinity under the conditions of manufacture. It consists essentially of calcium hydroxide, or of a mixture of calcium hydroxide and magnesium oxide or hydroxide.

(c) **PACKING.**—Limestone is shipped in bulk in carload lots, or in cloth or paper bags. Quicklime is shipped either in bulk in carload lots or barrels holding 180 pounds net or 280 pounds net each. Hydrated lime is shipped in paper bags holding 50 pounds net each.

2. REQUIREMENTS

(a) **QUALITY.**—Except for the constituents enumerated below, the composition of a limestone, lime, or hydrated lime may vary

within wide limits and still be satisfactory to the glass manufacturer. Either high calcium or high magnesium material may be used. It is essential, however, that the composition be reasonably uniform from day to day. Otherwise the difficulty of controlling the process of manufacture would become too great.

(b) COMPOSITION.—Quicklime shall not contain more than 3 per cent CO_2 as shipped. Hydrated lime shall not contain more than 5 per cent CO_2 as shipped, and shall contain sufficient water to meet the chemical requirements of the calcium oxide.

Limestones, quicklimes, and hydrated limes may be divided into three classes, depending upon the character of glass for which they are suitable. To meet these specifications, the constituents listed below shall not exceed the maximum percentages nor fall below the minimum percentages given in the following table:

TABLE 1.—Composition of the Nonvolatile Portion of Limestone, Quicklime, or Hydrated Lime

Ingredients	Class 1		Class 2		Class 3	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
$\text{CaO}+\text{MgO}$		96		91		83
Ferric oxide	0.2		0.4		0.8	
Sulphuric and phosphoric anhydrides	1.0		1.0		1.0	
Silica	4.0		9.0		17.0	
Alumina	3.0		5.0		5.0	

The sum of the calcium and magnesium oxides is specified in the above table. In order to prevent undue variation in the relative proportions of these two ingredients the per cent calcium oxide shall be established by contract, and it is specified that the per cent calcium oxide shall not vary more than 2 per cent either way from the contract figure.

An approximate figure for the content of alumina should also be included in the contract. This figure must come within the limits set in the above table, and it is specified that the amount of alumina in the material delivered shall not vary more than 1 per cent either way from the contract figure.

(c) FINENESS.—Unless otherwise specified, limestone, quicklime, and hydrated lime shall be crushed so that all will pass a No. 16 sieve.

NOTE.—A No. 16 sieve has an opening of 1.19 mm and a wire diameter of 0.54 mm, with a permissible tolerance of 2 per cent in the opening and 10 per cent in the wire diameter.

(d) MARKING.—Each carload of material, or fraction thereof, shall be legibly marked with the names of the consignor and consignee, and with some means of identifying the particular contract on which the shipment is made.

This information is in addition to that required by the Federal lime-barrel law.

(e) RETESTING.—Notice of the rejection of a shipment based on these specifications must be in the hands of the consignor within 10 days after the receipt of the shipment at the point of destination. If the consignor desires a retest, he shall notify the consignee within 5 days of receipt of the notice of rejection. The consignee shall provide all reasonable facilities to permit the consignor to resample the material. This retest shall be at the expense of the consignor.

3. SAMPLING AND TESTING

(a) SAMPLING.—The purchaser will bear all expense of sampling and testing. When limestone or quicklime is shipped in bulk, the sample shall be so taken that it will represent an average of all parts of the shipment from top to bottom, and shall not contain a disproportionate share of the top and bottom layers, which are most subject to changes. The sample shall consist of 1 shovelful for each 3 tons of material, but not less than 10 shovelfuls, taken from different parts of the shipment. The total sample taken shall weigh at least 100 pounds, shall be mixed thoroughly, and “quartered” to provide a 15-pound sample for the laboratory. In case a shipment consists of more than one car, a separate sample shall be taken from each car.

When quicklime is shipped in barrels, at least 3 per cent of the number of barrels shall be sampled. They shall be taken from various parts of the shipment, dumped, mixed, and sampled as specified in the above paragraph.

In the case of hydrated lime, the sample shall be a fair average of the shipment. Three per cent of the packages shall be sampled. The sample shall be taken from the surface to the center of the package. The material so obtained shall be thoroughly mixed and quartered to provide a 2-pound sample for the laboratory.

When sampling quicklime or hydrated lime, it is essential that the operation be conducted as expeditiously as possible, in order to avoid undue exposure of the material to the air. The sample to be sent to the laboratory shall immediately be placed in an air-

tight container in which the unused portion shall be stored until the shipment has been finally accepted or rejected by the purchaser.

The sample may be taken either at the point of shipment or at the point of destination, as agreed upon by the contracting parties. If it is desired to enforce the requirement as to carbon dioxide, the sample must be taken at the point of shipment.

(b) TESTING.—The following directions are a brief summary of the analytical methods which are recommended. For more complete information on this subject references should be made to "The analysis of silicate and carbonate rocks," by W. F. Hillebrand, United States Geological Survey Bulletin No. 700.

Blast 0.5 g of the sample for 15 minutes in a platinum crucible. Cool and transfer to an evaporating dish. Mix to a slurry with distilled water. Add 5 to 10 cc concentrated HCl. Heat gently until solution is complete, breaking up lumps if necessary. Evaporate to dryness on water bath. Add 5 to 10 cc concentrated HCl and dilute with an equal volume of distilled water. Digest on water bath for 10 minutes. Filter and wash with hot water. Evaporate the filtrate to dryness. Dissolve in acid and water as before. Filter, and wash with hot water. Ignite the two precipitates together and weigh as silica and insoluble matter.

Dilute the above filtrate to 250 cc. Add HCl if necessary to insure a total volume of 10 to 15 cc. Make alkaline with NH_4OH . Boil until odor of NH_3 is barely noticeable. Filter, and wash slightly with hot water. Dissolve the precipitate with hot dilute HCl and repeat the precipitation as before. Filter and wash thoroughly with hot water. Ignite and weigh as oxides of iron, aluminum, and phosphorus.

To the filtrates from the above add a few drops of NH_4OH and bring to a boil. Add 25 cc of a saturated solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Continue boiling until the precipitate becomes granular. Let stand until precipitate settles clear. Filter, and wash with boiling water. Ignite the precipitate, dissolve in dilute HCl, and dilute to 100 cc. Add excess of NH_4OH , and boil. Filter out any insoluble matter, ignite and weigh, and add its weight to the oxides of iron and aluminum found previously. To this filtrate add $(\text{NH}_4)_2\text{C}_2\text{O}_4$, proceeding as before. Filter, and wash with boiling water. Ignite, and blast to constant weight as calcium oxide.

Acidify the filtrates from the above with HCl. Evaporate to 150 cc. Add 10 cc of a saturated solution of $\text{NaNH}_4\text{HPO}_4$ and boil. Cool. Add NH_4OH drop by drop, with constant stirring,

until the precipitate starts to form. Then add moderate excess of NH_4OH . Stir for several minutes. Let stand overnight. Filter, and dissolve the precipitate in hot dilute HCl . Dilute to 100 cc, add 1 cc of saturated solution of $\text{NaNH}_4\text{HPO}_4$, and precipitate as before. Filter, and wash with an alkaline solution made by diluting NH_4OH until it contains about 2.5 per cent NH_3 and then add a few drops of HNO_3 . Ignite, and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$. Multiply this weight by 0.3621 to find the weight of MgO .

Place 5 g of the sample of quicklime or hydrated lime, or 0.5 g of limestone, in a small Erlenmeyer flask and cover with hot distilled water. Connect this flask into a carbon-dioxide train, set up as follows: Next to the flask is a reflux condenser, to which is connected a calcium-chloride drying tube, followed by a tube containing anhydrous CuSO_4 , then another tube of CaCl_2 , then by two tubes filled with soda lime, and finally by another tube of CaCl_2 . The entire train must be so arranged that a stream of CO_2 free air can be kept passing through it. Start this stream of air. Weigh the tubes containing soda lime and replace them in the train. Add to the sample in the flask about 25 cc of 1:1 HCl , being careful that no gas is lost and that the effervescence is not too violent during the operation. When the effervescence diminishes, heat the flask, bringing the liquid gradually to boiling. Boil for 10 minutes. Remove the flame and allow the flask to cool while the stream of air is still flowing, for 15 minutes. Disconnect and weigh the soda-lime tubes. Their increase in weight is recorded as carbon dioxide.

Dissolve 5 g of the sample in HCl and evaporate to dryness. Dissolve the residue in HCl , filter, and wash with hot water. Fuse the residue with Na_2CO_3 . Treat the filtrate with NaOH in boiling solution, filter, and wash with hot water. Dissolve both this precipitate and the fused residue in dilute H_2SO_4 . Reduce with Zn and titrate with $\frac{N}{20} \text{KMnO}_4$. Calculate the result to per cent Fe_2O_3 .

Dissolve 2 g of the sample in 10 cc water and 15 cc 1:1 HCl . Filter out insoluble matter. Dilute filtrate to 250 cc. Heat to boiling and add 10 cc of a boiling 10 per cent solution of BaCl_2 , drop by drop, with constant stirring. Let stand overnight, filter, wash with hot water, ignite, and weigh as BaSO_4 . Calculate to per cent SO_3 .

Dissolve 10 g of the sample in 80 cc of 1:1 HNO_3 . Filter, wash, fuse the residue with Na_2CO_3 , dissolve the melt in HNO_3 , and add this solution to the filtrate. Boil the filtrate with 10 cc of 1.5 per cent KMnO_4 solution until MnO_2 is precipitated. Add enough H_2SO_4 to dissolve the MnO_2 . Neutralize with NH_4OH . Add 1 cc of concentrated HNO_3 for every 100 cc of solution. Bring to 40°C and precipitate with ammonium molybdate. Shake for 10 minutes and let stand at 40°C for 12 hours. Filter and wash with 1 per cent KNO_3 . Dissolve the precipitate in a known volume of $\frac{N}{10}$ NaOH and CO_2 free water. Titrate the excess NaOH , using phenolphthalein as indicator. Calculate the per cent P_2O_5 , using the proportion, $\text{P}:\text{NaOH} = 1:23$.

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